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SURFACE COOLED BY LIQUID NITROGEN AT GAS
TEMPERATURES RANGING FROM 136°K to 548°K

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dioxid bei Gastemperaturen von 136°K bis 548°K
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THE PUMPING SPEED FOR CARBON DIOXIDE BY THE ACTION OF A
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ABSTRACT: This paper covers a brief description of the measuring equipment concerning the pumping speed for carbon dioxide by the action of a surface cooled by liquid nitrogen at gas temperatures ranging from 136°K to 548°K, and the discussions of the measuring results for pressures ranging from $6 \cdot 10^{-7}$ Torr up to $8 \cdot 10^{-5}$ Torr. It also presents theoretical deliberations on the relation of the pumping speed of cryosurfaces with the thermal conductivity of the condensed gas layer. It is thus possible, after the constants have been determined, to predict the pumping speed of cryosurfaces in vacuum, within certain limits, also for other temperatures of the cryosurface and the condensing gas. The measuring results obtained hereby as well as those published by DAWSON and HAYWOOD [sic] prove a good relationship with the theoretical considerations.

List of Abbreviations and Symbols

| | | |
|--------------------|--|------------|
| E_{total} | = total energy of gas particles (in relation to those in condensate) in cal/mol | <u>/6*</u> |
| E_{kin} | = kinetic energy of gas particles in cal/mol | |
| E_{kin}^* | = kinetic energy of gas particles still captured by the cryosurface in cal/mol | |
| H_{evap} | = heat of evaporation in cal/mol | |
| W | = energy absorbed by condensate upon impinging of gas particles in cal/mol | |
| λ | = conductivity of condensate in cal/sec/cm/° | |
| c | = constant | |
| α | = probability of adherence | |
| n/n_0 | = ratio of particles with energy less than E_{kin}^* to total particles | |
| k | = Boltzmann constant | |

*Numbers in the margin indicate pagination in the foreign text.

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|-----------------|--|
| R | = gas constant in cal/°/mol |
| M | = molecular weight |
| m | = molecular mass |
| v | = velocity of gas particles in m/sec |
| T | = gas temperature in ° |
| T* | = cryosurface temperature in ° |
| W _{ad} | = probability of evaporation |
| A | = constant |
| Φ _{ad} | = heat of evaporation and/or absorption in cal/mol |
| t | = pressure in Torr |
| d | = constant |

1. Introduction

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The present investigations of the pumping speed for a carbon dioxide of different gas temperatures of cryosurface exposed to liquid nitrogen are a continuation of DVL-Report No. 320 [9] in which the gas temperature was kept constant (at room temperature) and the cryosurface temperature varied between 68 and 95°K. Interpretation of the findings of the first report indicated that the probability of adherence is determined in a first approximation by the gas temperature and the thermal conductivity of the condensate. It therefore seemed obvious to test the validity of the relation derived from this for various gas temperatures. Let us briefly review the derivation of the formula:

Upon impinging upon the condensate surface (type-specific substrate), the gas particles transmit a certain energy (W) through collision. Evidently, a gas particle can escape to the gas space after the collision only then when its residual energy is still higher than the heat of evaporation (H_{evap}) at the existing cryosurface temperature.

In relation to the condensate, a particle in the gas space has the energy of evaporation and also the kinetic energy E_{kin} (disregarding the component of rotation and oscillation as well as the heat content of the condensate): It is now assumed that the energy W transmitted to the condensate upon impinging of the gas particles, is in first approximation proportional to the total energy E_{total} and also to the conductivity λ of the condensate at the cryosurface temperature: It is further assumed that the thermal conductivity in first approximation represents a scale for the exchange of heat between gas particles and condensate. A temperature gradient in the condensate layer between condensate surface and cryosurface is not required for validity of Eq. 2. It is instead assumed here that the temperature at the condensate surface is not

appreciably different from the metal of the cryosurface. The thermal conductivity is intended to express the extent to which the atoms of the condensate in immediate proximity of the point of impingement of a gas particle are able to absorb the applied energy. This is evidently a great simplification of the very complicated condensation processes so that deviations must necessarily be expected.

Those gas particles no longer possessing the energy of evaporation after collision are although they do not escape into the gas space - by no means already incorporated in the crystal bond of the condensate. However, it is not intended here to enter into these phenomena. In regard to the cryopump, it is important that the gas particles are removed from the gas space.

$$E_{\text{total}} = E_{\text{kin}} + H_{\text{evap}} \quad (1)$$

$$W = c \cdot \lambda \cdot E_{\text{total}} \quad (2)$$

However, let us return to the considerations outlined initially. Since / 8 it is assumed here that the impinging gas particles do not obtain any appreciable energy for evaporation from the condensate -- in contrast to the derivation for the relation obtained for equilibrium of absorption and/or condensation -- there are captured obviously, in the field of force of the surface atoms, those gas particles for which

$$E_{\text{total}} - W \leq H_{\text{evap}} \text{ or with (1)} \quad (3)$$

$$(H_{\text{evap}} + E_{\text{kin}}^*) - W \leq H_{\text{evap}} \text{ or} \quad (4)$$

$$E_{\text{kin}}^* \leq W. \quad (5)$$

With Eq. 2, we obtain:

$$E_{\text{kin}}^* \leq c \cdot \lambda \cdot (H_{\text{evap}} + E_{\text{kin}}) \text{ or} \quad (6) \quad \text{/ 9}$$

$$E_{\text{kin}}^* \leq \frac{c \cdot \lambda \cdot H_{\text{evap}}}{1 - c \cdot \lambda} \quad (7)$$

This consequently signifies that all gas particles whose kinetic energy exceeds the value obtained from this relation, will return into the gas space. We now desire to know what fraction $\alpha = n/n_0$ of the total active gas particles has a kinetic energy which does not exceed the value from Eq. 7 since this will be evidently also the probability of adherence α .

From the Maxwell distribution of velocity at a gas temperature T is calculated the number of particles in whose velocity lies in the range v and $v + dv$, as

$$dn = n_0 \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{\frac{2}{3}} \cdot v^2 \cdot e^{-\frac{mv^2}{2kT}} \cdot dv \quad (8)$$

Integration furnishes all particles whose velocity does not exceed a given value v_0 , and/or, by division through n_0 , the fraction:

$$\frac{n}{n_0} = \alpha = \frac{4}{\sqrt{\pi}} \cdot \left(\frac{m}{2kT}\right)^{\frac{2}{3}} \cdot \int_0^{v_0} v^2 \cdot e^{-\frac{mv^2}{2kT}} \cdot dv \quad (9)$$

This equation can be directly solved by partial integration; accordingly

$$\frac{n}{n_0} = d \left[-u \cdot e^{-u^2} + \int e^{-u^2} \cdot du \right]_0^{u_0}, \quad (10)$$

where u^2 has been introduced for $mv^2/2kT$ and the factors have been grouped in the constant d .

$$\int e^{-u^2} \cdot du$$

is the Gauss integral of error. In Eq. 10, we still need to determine the limit value u_0 , i.e. /10

$$u_0 = \sqrt{\frac{mv_0^2}{2kT}} = \sqrt{\frac{E_{kin}^*}{RT}}, \quad (11)$$

where we expanded the sq. root on the right with the Loschmidt number. In Eq. 11, E_{kin}^* must be determined from Eq. 7 for the respective type of gas.

The constant c in Eq. 7 must be determined experimentally; this was done here from the measured probability of adherence for a liquid-nitrogen temperature (77°K of the cryosurface) and the gas temperature 296°K (room temperature).

It should be pointed out here that, for low gas temperatures, i.e. those only slightly higher than the temperature of the cryosurface, the probability of adherence does tend toward 1 but does not exactly attain this value. This is due to the velocity distribution since there are, even at lower temperature, still a finite number of particles with arbitrarily high velocity - from the Maxwell distribution. Although this is still comprehensible, it must definitely be emphasized that we then closely approach the conditions for equilibrium of absorption and/or condensation and consequently the formula indicated in [2] is more appropriate for the real conditions. (It should be taken into account that a part of the impinging gas particles obtains the energy required for evaporation from the condensate). It will be pertinent to also restate the Frankel formula:

$$W_{ad} = A \cdot e^{-\frac{\Phi_{ad}}{kT^*}} \quad (12)$$

where W_{ad} = probability of evaporation; A = constant only slightly variable through temperature in comparison with the exponential function; Φ_{ad} = heat of evaporation and/or absorption.

2. Description of Apparatus

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Since the gas temperature had to be varied for these investigations, the original chamber could not be utilized which proved in any event to be somewhat too cumbersome. We utilized the same pump installation but the T-connection now serves also as receiver. The inner diameter was 250 mm with a height of about 600 mm (Fig. 1). The inner cylinder required for varying the gas temperature and the cryosurface were mounted on the upper flange. In order to vary the temperature of the cylinder, it was surrounded with cooling and/or heating coils. In order for the temperature differential between intake and discharge circuit to have as little effect as possible on the cylinder itself, both circuits were arranged side-by-side on the cylinder.

The cooling trap was made of high-grade steel with a diameter of 9 cm and a height of 8 cm. In order to provide for uniform temperature, a silver plate, 1.5 mm thick, was brazed to the bottom of the cooling trap which constituted the cryosurface in these investigations.

In the upper cover of the inner cylinder, an aperture with a diameter of 8 cm had been provided as access to the cryosurface (consequently, the cooling trap had a projecting edge of 0.5 cm). The distance between cryosurface and cover was 0.4 to 0.5 mm. The distance was selected so small so that re-evaporating gas particles - on the side wall of the cooling trap which always occurs due to the drop of level of the liquid nitrogen - would fully condensate in this ring gap and consequently not distort the measurements. This surface is small in relation to that of the cryosurface.

Since the ionization manometers are operated at room temperature, the connection to the copper cylinder was provided by a pipe with a diameter of 4.5 cm and a length of 20 cm. The pipe was attached to the upper flange and had approximate room temperature. The gas particles reaching the ionization manometer through this pipe, consequently also assumed room temperature. The admittance is so high that no error of measurement needs to be anticipated from the pumping action of the ionization manometer. In order to test for any impurities, we also connected a mass spectrometer by means of a branch connection in the proximity of the ionization manometer.

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The principle of the gas intake was retained, i.e. the volume of gas admitted could be varied across a Granville-Phillips valve and the actual volume was determined from the admittance of an opening (diameter 1 cm) and the pressure differential ahead and beyond the opening. The indication of the ionization manometers on the intake-side and the pump-side was compared with the valve to the diffusion pump closed. The admittance ["Leitwert"] was so high that,

with the existing leakage rate (+ gas delivery), no appreciable pressure differential between intake tank and pump space could be maintained. The comparison was made with nitrogen and/or, with a warm cooling trap, with carbon dioxide.

The gas temperature was varied by heating and/or cooling of the inner copper cylinder. The heating coils were connected to a thermostat. Cooling was effected with nitrogen from pressure tanks conducted through a copper-tube coil cooled with liquid nitrogen from the outside. The temperature of the nitrogen was varied by different depth of submersion of the coils in the liquid-nitrogen bath.

The temperature of the inner copper cylinder was measured by thermo-couple elements at three points. The highest deviation was 6° which is negligible.

Unfortunately not all flange connections of the apparatus could be provided by gold gaskets so that "VITON" gaskets were used in some cases. It was consequently not possible to heat the installation to more than between 180 and 220 $^{\circ}\text{C}$. After heating, the vacuum was about 1×10^{-8} Torr and dropped, under cooling of the cryosurface, within the copper cylinder to about 6 to 7×10^{-9} Torr.

Outside of the copper, 3 to 4×10^{-9} Torr were measured. At measurements with high cylinder temperature (for high gas temperature) the discharge vacuum was not as satisfactory but still always better than 1×10^{-7} Torr.

The temperature of the cryosurface was not specially measured but equated with that of the boiling nitrogen. In order to provide approximately the same conditions on the intake side of the ionization manometer as of the side toward the cryopump, a copper pipe with a diameter of 4.5 cm and a length of 20 cm was here also placed ahead of the manometer.

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During the measurements, the UHV-valve to the diffusion pump was left open (and/or half closed) so that no enrichment of non-condensable gases would occur.

The pump installation consisted of an oil-diffusion pump (capacity 2,000 lit/sec), baffles cooled by water and "Frigen", and a Roots rotary tandem pump as booster pump.

The integral leakage rate (plus gas delivery) was determined from the pressure rise in time with closed UHV-valve as 1.6×10^{-7} Torr.

3. Measuring Method

After the copper cylinder remained at constant temperature, we began to measure absorptivity. We initially admitted a small volume of gas which was then increased in steps. Each time, the stationary state was observed for 2 to 3 minutes before increasing the volume of gas admitted for further measurement of absorptivity. The indication of the ionization manometers was recorded in each case 3 to 4 times for a given volume of gas admitted. However, it remained practically the same.

In one series of measurements, the lowest pressure at which absorptivity was determined, ranged between 10^{-7} to 10^{-6} Torr and the highest pressure around 10^{-5} Torr but always below 1×10^{-4} Torr. The probability of adherence was determined from the main value for the various pressures.

Measurement of absorptivity for a constant gas temperature lasted about 15 to 25 minutes. Even for measurements at high gas temperatures, it was not necessary to refill the cooling trap with liquid nitrogen during the test period. However, the findings here were less reproducible.

4. Discussion and Evaluation of Findings

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Since pressure measurement took place at room temperature and not at the gas temperature for which the absorptivity had just been determined, the values had to be converted. According to Knutsen, the pressure in both tanks is not constant under the given conditions, i.e. two connected vessels with different temperature in the region of molecular flow, but the number of particles flowing in each case from one into the other container must instead be equal.

$$N_1 \cdot \bar{v}_1 = N_2 \cdot \bar{v}_2 ; \rightarrow N_1 \cdot \sqrt{\frac{2kT_1}{\pi m}} = N_2 \sqrt{\frac{2kT_2}{\pi m}} , \quad (13)$$

$$p_1 \cdot V = N_1 \cdot k \cdot T_1 , \text{ becomes:} \quad (14)$$

$$p_1 = p_2 \sqrt{\frac{T_1}{T_2}} . \quad (15)$$

In consideration of Eq. 15, the data were evaluated and grouped for the individual temperatures in Fig. 2 to 7. Fig. 8 shows the probability of adherence as a function of gas temperature. The solid-line curve represents the dependence calculated from Eq. 10 where the component of rotation and oscillation was not taken into account. If this additional energy is taken into account we obtain lower values, i.e. 25% at a gas temperature of 500 °K. Fig. 8 indicates that the findings agree well with the calculated dependence on temperature. It cannot yet be definitely stated whether this relation is no longer valid for higher gas temperatures or whether it involves an error of measurement.

At lower gas temperatures, agreement is better. However, the fact that all values are somewhat lower (below 200 °K) is probably due to the fact that the re-evaporating component has not been taken into account, i.e. those particles which obtain, from the condensate, the energy required for evaporation. The probability of adherence as a function of gas temperature found by us signifies, however, that the concept according to which all gas particles encountering the cryosurface are absorbed, it is here not applicable because the probability of adherence would otherwise remain independent of the gas temperature.

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The agreement of the measured findings with those of Dawson and Haywood [sic] can be regarded as satisfactory. The dependence of the probability of adherence on the temperature of the cryosurface found previously is also represented for better understanding (Fig. 9). The conductivity of the condensate was determined by the empirical relation indicated by [4].

$$\lambda_{CO_2 \text{ solid}} = 216 / T^{1.236}.$$

Let us here point out also that the probability of adherence as given by Eq. 10 again decreases under certain circumstances for extreme low temperatures (liquid helium) of the cryosurface because the conductivity at these temperatures drops again with decreasing temperature which, according to these concepts, results in a reduction of the exchange of energy between gas particle and condensate surface.

5. Summary

The measured data agree well with the values of Dawson and Haygood [sic]. The theoretical considerations have also been confirmed satisfactorily (to about 400 °K) although the assumptions made no longer seemed to apply for higher gas temperatures (about 500 °K). For this, the measured data are affected by relatively high errors. The dependence of the probability of adherence on gas temperature signifies, however, that the particles again escaping into the gas space do not obtain the required energy of evaporation through random statistical energy accumulation from the condensate. To what extent these considerations can be transposed to other gases and cryosurface temperatures will need to be further investigated in detail.

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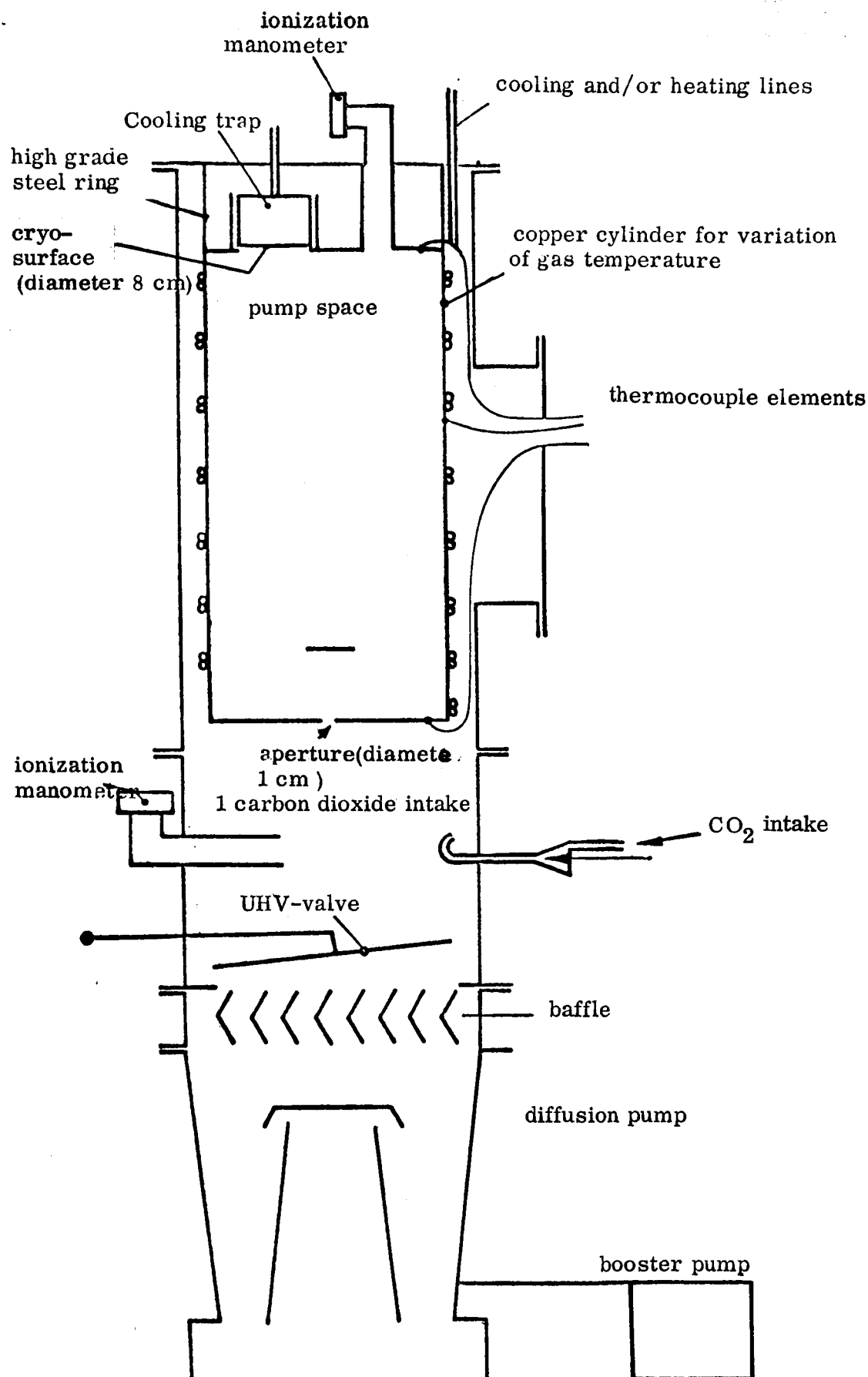


Figure 1 Diagram of Experimental Installation.

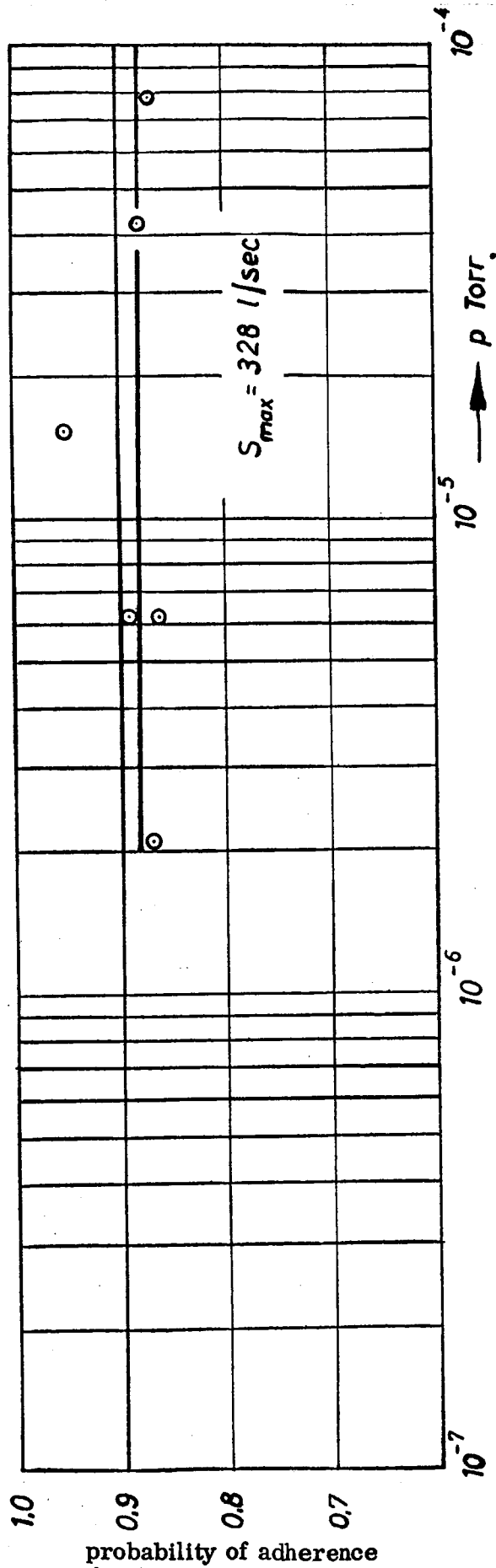


Figure 2 Probability of Adherence for Carbon Dioxide (136 °K) on an Cryosurface (77°K).

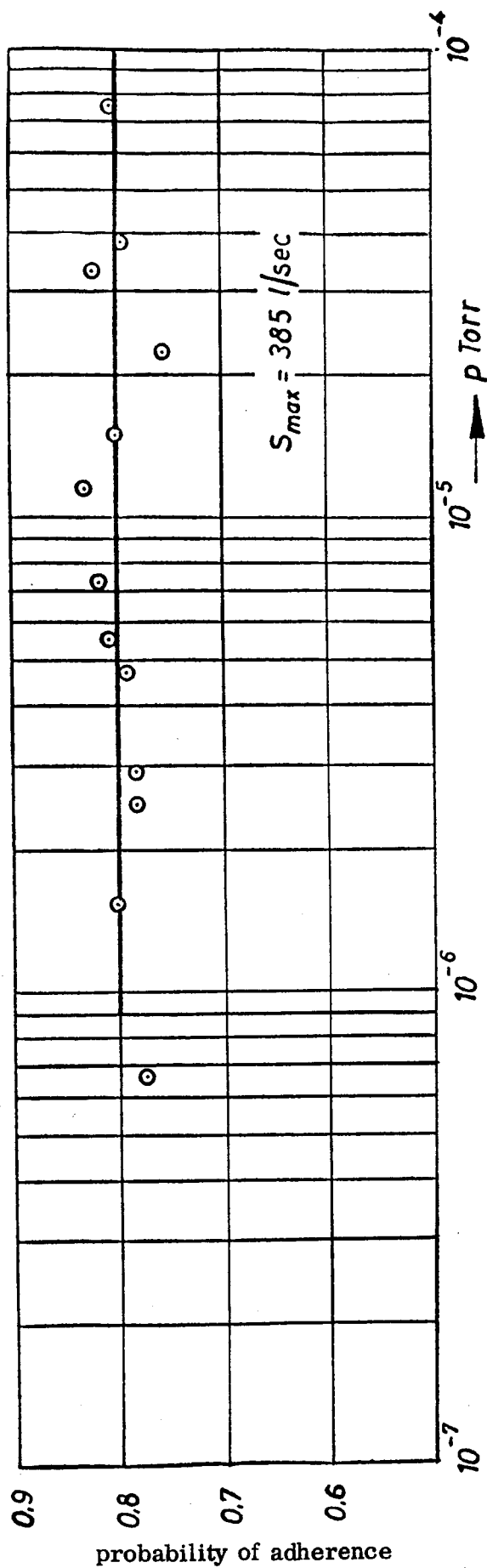


Figure 3. Probability of Adherence for Carbon Dioxide (187 °K) on an Cryosurface (77°K).

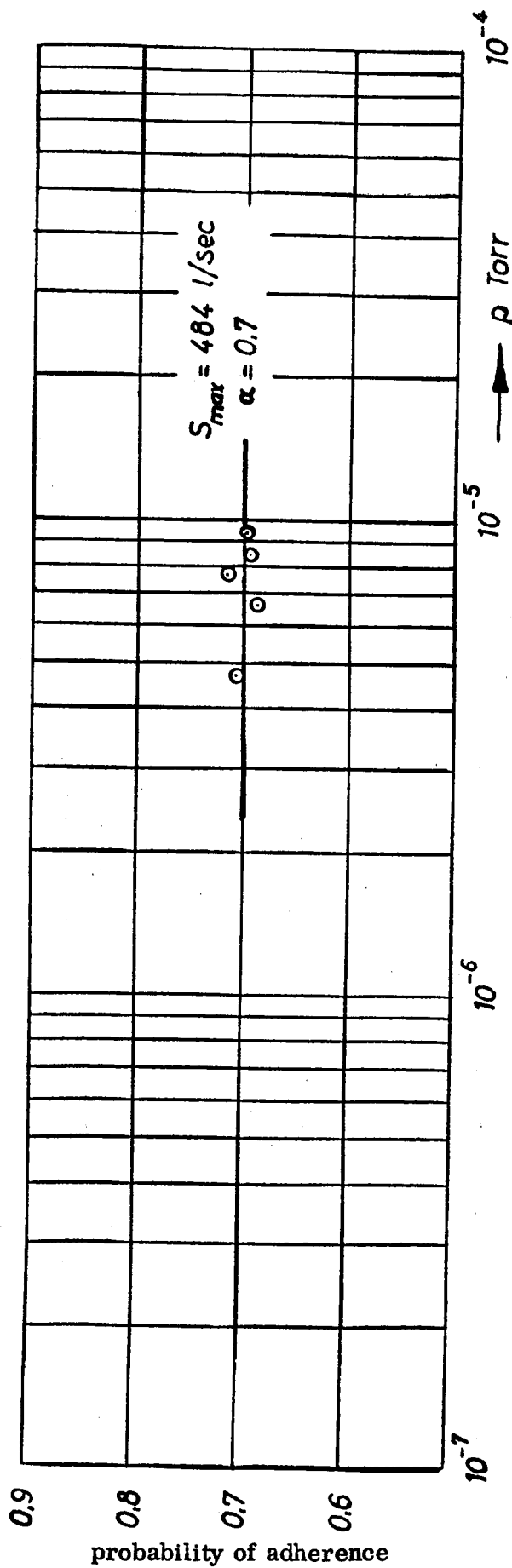


Figure 4. Probability of Adherence for Carbon Dioxide (296 °K) on an Cryosurface (77°K).

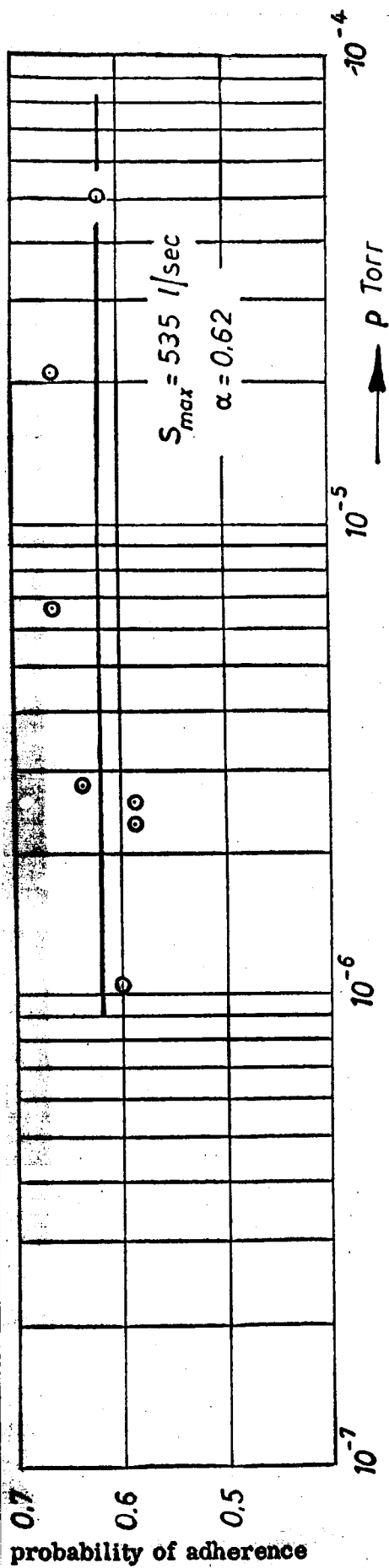


Figure 5. Probability of Adherence for Carbon Dioxide (361 °K) on an Cryosurface (77°K).

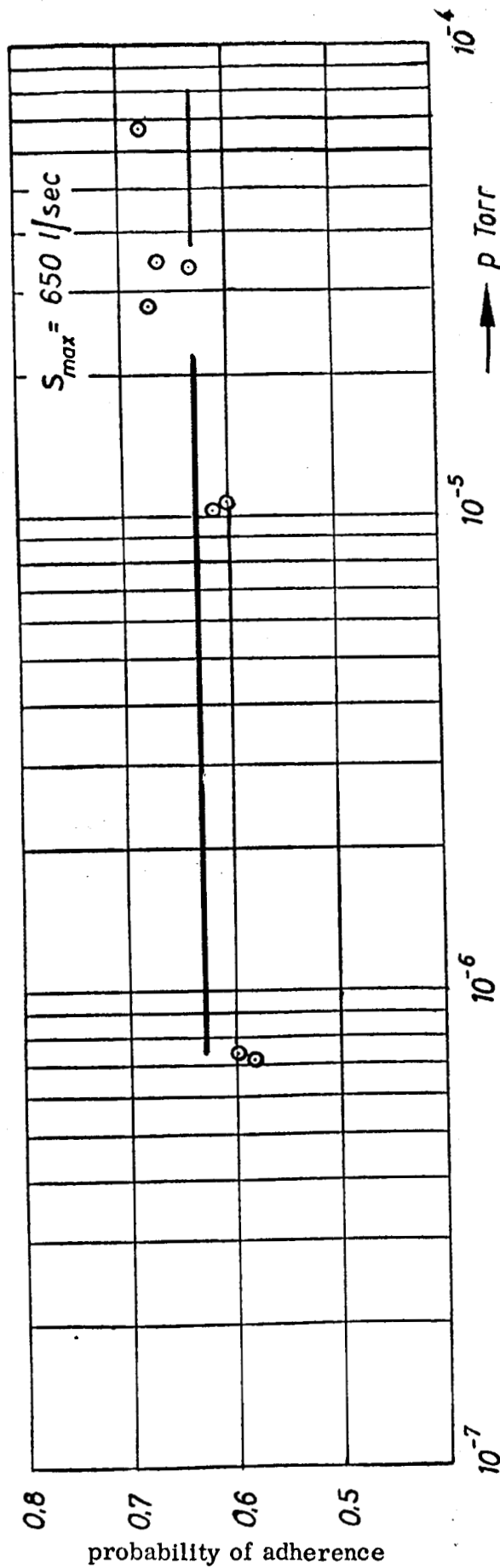


Figure 6. Probability of Adherence for Carbon Dioxide (529°K) on an Cryosurface (77°K).

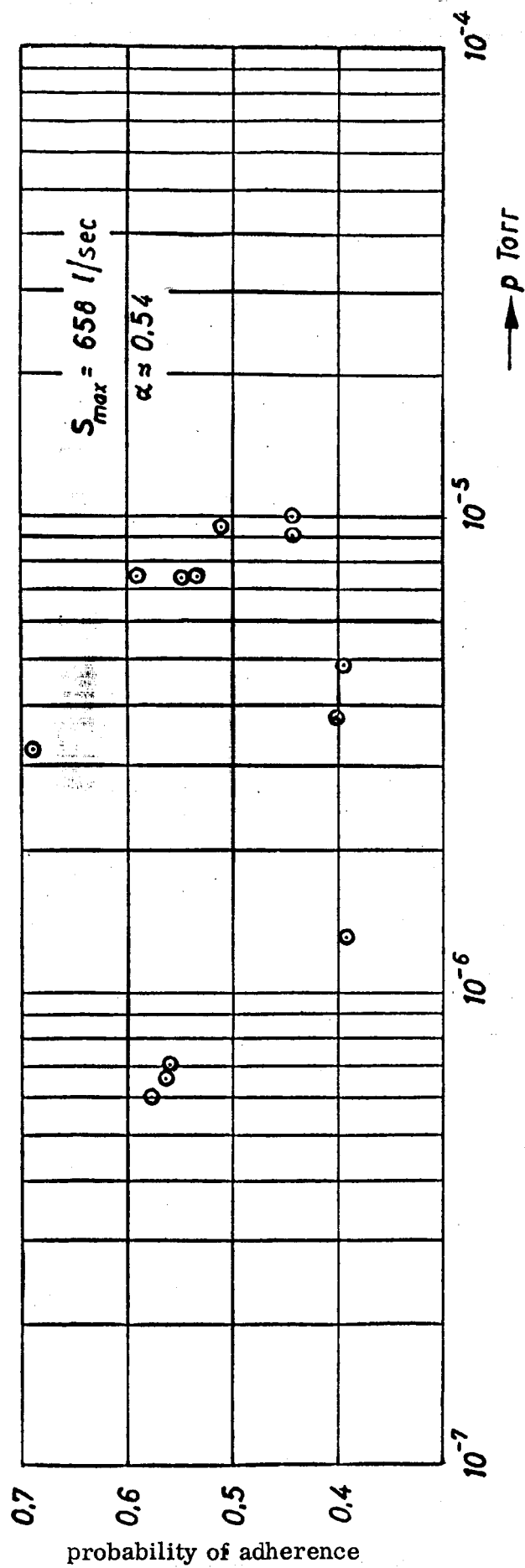


Figure 7. Probability of Adherence for Carbon Dioxide (548 °K) on an Cryosurface (77°K).

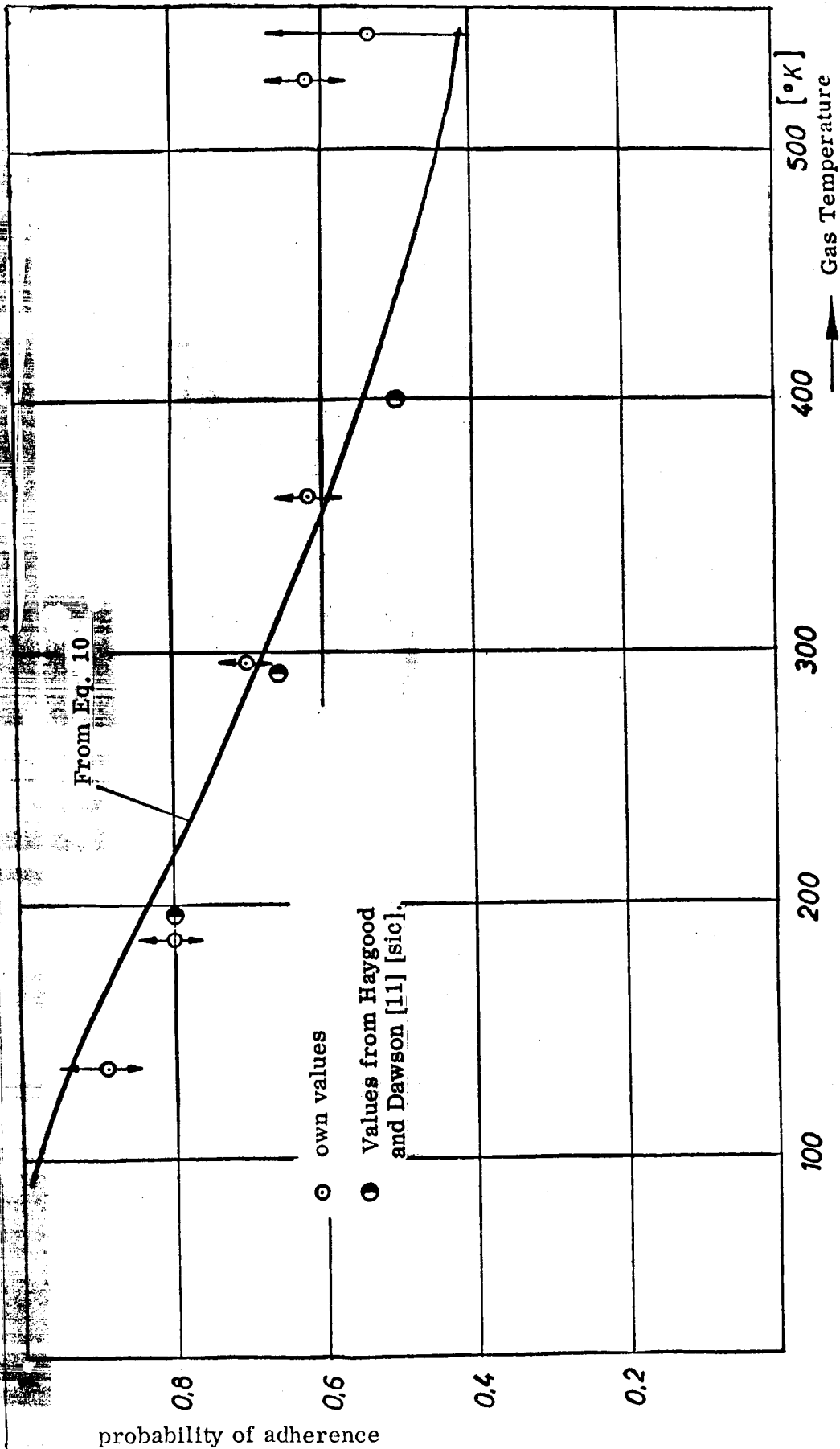


Figure 8. Probability of Adherence as a Function of Gas Temperature.

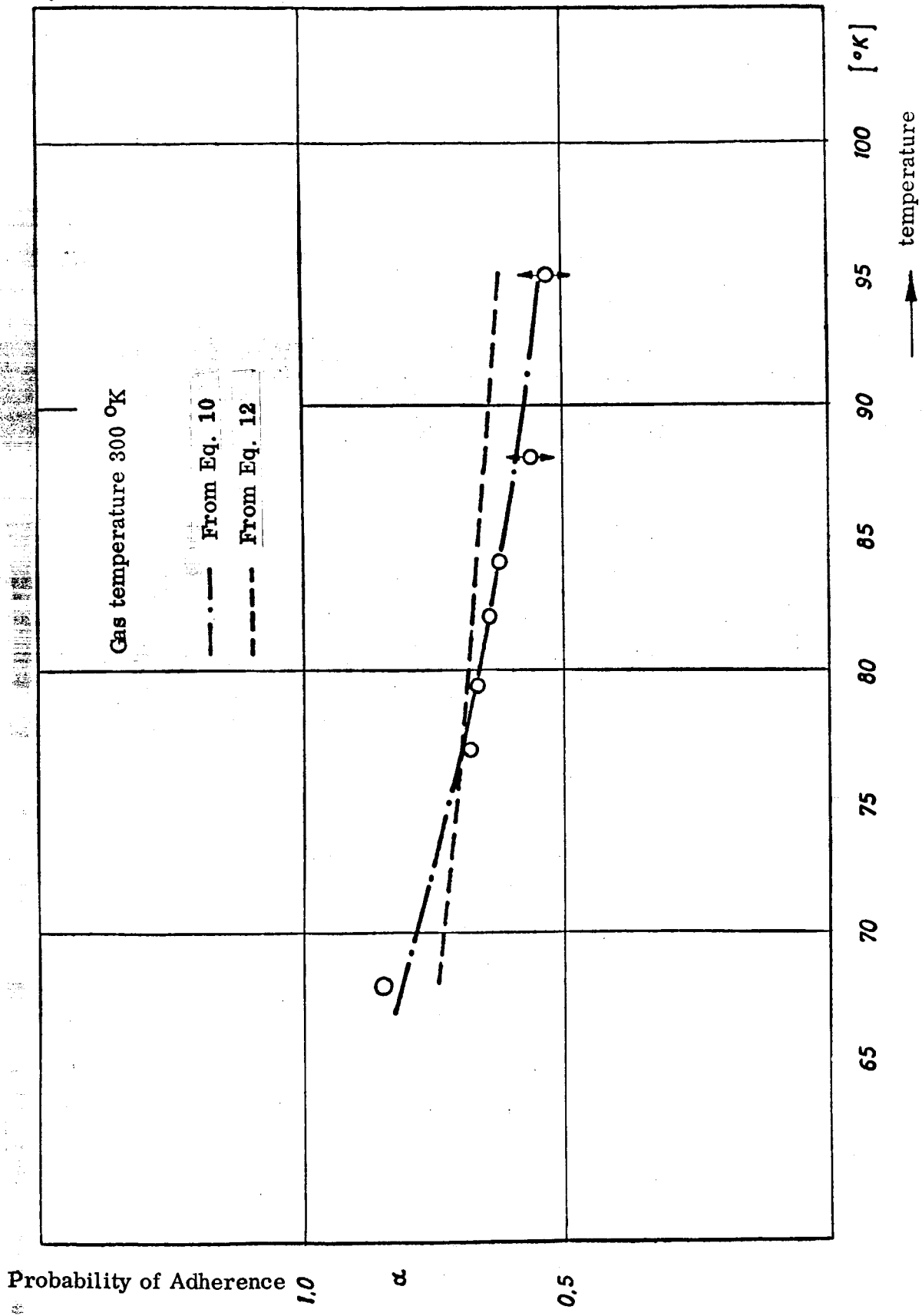


Figure 9. Probability of Adherence for Carbon Dioxide as a Function of Cryosurface Temperature.